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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT - 80-0002

JANUARY 1980

LiSi AND LiB AS ANODES IN CHLOROALUMINATE THERMAL CELLS

CAPT ROBERT L. VAUGHN

PROJECT 2303

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AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

FJSRL-TR-80-0002

This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F2-07, "Pelletized Thermal Batteries". Captain Robert L. Vaughn was the Project Scientist in charge of the work.

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This report has been reviewed by the Chief Scientist and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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Lithium silicon (40 weight percent Li) and lithium boron were studied as anode materials in chloroaluminate thermal cells and were compared with lithium aluminum. Lithium boron anodes were tested only at a single temperature (200°C) because of low availability whereas lithium silicon was studied over the temperature range 175 to 275°C. The current density range was 15 to 150 mA/cm². 50 cm

The results showed that lithium silicon behaved like lithium aluminum, with linear polarization over the current densities studied. The internal resistances

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sq cm

were the same at all temperatures. On the other hand, lithium boron displayed an activation overpotential at current densities less than 50 mA/cm^2. At higher current densities, an internal resistance of less than 0.1Ω was indicated for the lithium boron-anode cells.

OMEGA

This study shows that LiSi offers no advantage over lithium aluminum as an anode for chloroaluminate thermal cells. However, LiB promises to be a superior anode material at high current densities.

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LiSi AND LiB AS ANODES IN CHLOROALUMINATE THERMAL CELLS

By

Capt Robert L. Vaughn

TECHNICAL REPORT FJSRL-TR-80-0002

January 1980

Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
US Air Force Academy, Colorado 80840

PREFACE

This report documents work done under Work Unit 2303-F2-07, Pelletized Thermal Batteries, between 27 March and 21 September 1979. The author sincerely thanks Mr. Ralph Szwarc of General Electric Neutron Devices, Pinellas Park, FL for providing the LiB anodes used in this study.

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

Lithium alloys are used as anodes in molten salt batteries in order to reduce lithium reactivity and to improve lithium retention at operating temperatures. However, the specific energy is reduced due to the weight of the electrochemically inert component in the alloy.

Lithium alloys that have been extensively studied in molten salt media are LiAl (1) and more recently LiSi and LiB (2-4). The studies cited used LiCl-KCl eutectic as the electrolyte and measurements were made at temperatures from 377°C to 600°C. These alloys have also been tested in thermal batteries using the LiCl-KCl electrolyte. Bush showed that LiSi is superior to LiAl in the Li/LiCl-KCl/FeS_2 thermal battery (5), and Szwarc and co-workers demonstrated good performance using LiB in single cell tests (6).

LiSi and LiB both offer the advantage over LiAl of higher weight percent lithium, indicating an immediate increase in energy density for LiSi and LiB. LiB appears especially attractive because the alloy is thought to consist of free lithium metal contained in a LiB-compound matrix (4). However, James and DeVries indicated that the performance of LiB anodes fell off sharply below 450°C (5).

In our laboratory, we have tested lithium, aluminum, and LiAl alloys as anodes for chloroaluminate cells, especially thermal cells, operating at temperatures from 175°C to 275°C (7). The LiAl alloy 28 weight percent in lithium gave the best results.

In light of the inherent weight advantage of LiSi and LiB alloys and of the recent LiCl-KCl thermal battery work using these alloys, we decided to test these alloys in thermal cells using $NaAlCl_4$ electrolyte and compare their performances with LiAl. This report presents the results of the comparison study.

EXPERIMENTAL

The electrolyte preparation, cell fabrication, and single cell discharge experiments have been described previously (8), although cell fabrication was modified somewhat to accommodate the LiB anodes. The LiB anodes supplied by General Electric Neutron Devices Department consisted of 0.16g of alloy pressed on to a stainless steel substrate having an aluminum tab. The anodes were 2.86 cm in diameter. The remainder of the LiB cell was a two-layer, electrolyte/cathode pellet made in the usual way. The anode was held in contact with the electrolyte/cathode pellet in the single cell tester.

The LiSi alloy used in this study was 40 weight percent lithium. The alloy was obtained in powder form (-40 to 200 meshes) from Foote Mineral Company, and was used as received to make the usual three-layer, pressed pellet cells.

All anodes were tested with a $CuCl_2$ cathode consisting of electrolyte-binder mixture, $CuCl_2$, and graphite. The $CuCl_2$ was anhydrous, 51.3% Cl, obtained from Alfa-Ventron Corporation and was used as received.

The number of LiB anodes was limited, therefore the measurements using LiB cells were confined to a single temperature (200°C). Cells having LiSi anodes were discharged over the temperature range of 175 to 275°C. Each LiB or LiSi cell was tested against a paired LiAl cell having the same electrolyte and cathode compositions. Our previous LiAl anodes contained some electrolyte-binder mixture, so the LiB anodes were compared with LiAl anodes containing the electrolyte-binder mixture. The LiSi anodes could be fabricated easily without the addition of electrolyte-binder mixture, and they were compared with LiAl anodes made without the electrolyte-binder mixture. Figure 1 summarizes the configuration of the single cells tested.

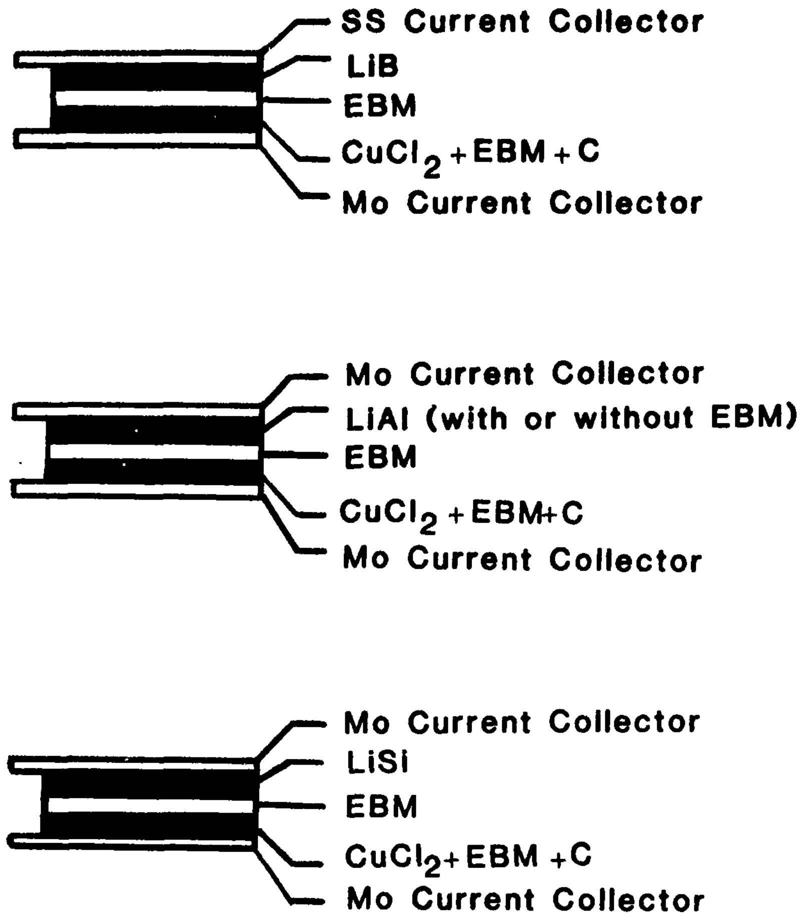

Figure 1. Cell configurations used for comparisons of different anodes. EBM denotes electrolyte-binder mixture (90 weight percent $NaAlCl_4$ + 10 weight percent SiO_2).

RESULTS AND DISCUSSION

LiB Anodes.

A total of six LiB anodes were tested at 200°C and current densities of from 15 to 100 mA/cm^2 (one cell shorted). Due to the limited number of anodes available the results are inconclusive.

The average open circuit potential of the six cells was 1.88V as opposed to 1.86V for the LiAl cells.

Figure 2 shows the linear polarization of LiAl-chloroaluminate cells. The internal cell resistance determined from the slope of this plot is 0.44Ω which agrees with earlier reports (9). Figure 3 shows that the polarization data for the LiB-chloroaluminate cells do not result in a straight line, but a logrithmic relation satisfying the equation

$$y = 1.539 - 0.118 \ln X$$

This behavior is characteristic of an activation overpotential as discussed by Bockris and Reddy (10). At higher current densities, the ohmic characteristics of the cell predominates, and the potential-current curve becomes linear with a slope related to the internal resistance. Figure 4 shows the same LiB polarization data with a linear regression line through the three points corresponding to the highest current densities (solid line). The slope of this line is 0.19Ω. This internal resistance is significantly lower than for LiAl cells indicating that LiB should be a superior anode material at higher current densities.

Figure 5 shows the energy densities for LiB and LiAl cells as a function of current density. The energy densities were measured to 80 percent of initial closed circuit voltage and were based on the total weight of the cell. The apparent superiority of the LiB cells can be attributed to the

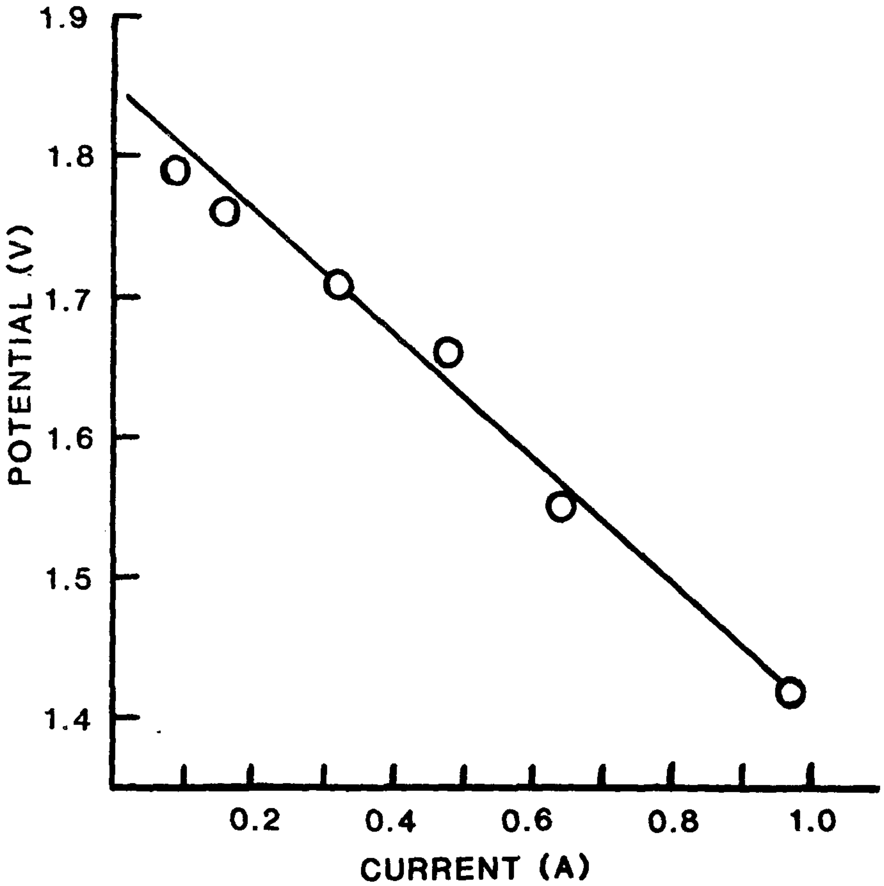

Figure 2. Polarization of LiAl/$NaAlCl_4$/CuCl2 thermal cells at 200°C.

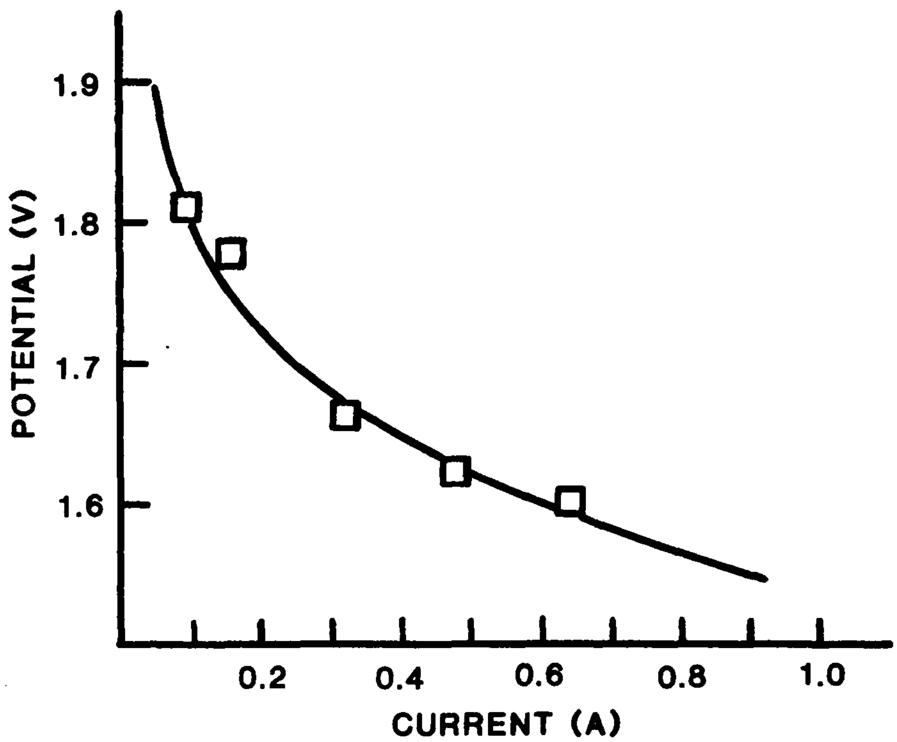

Figure 3. Polarization of LiB/$NaAlCl_4$/$CuCl_2$ thermal cells at 200°C.

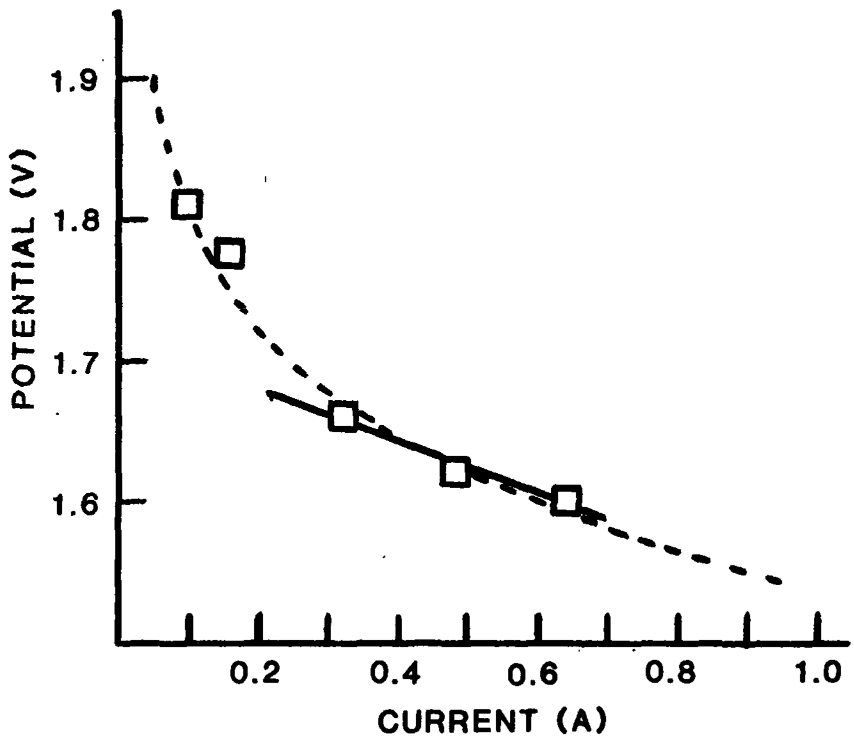

Figure 4. Polarization of $LiB/NaAlCl_4/CuCl_2$ thermal cells (broken line) showing the linear region at higher current densities.

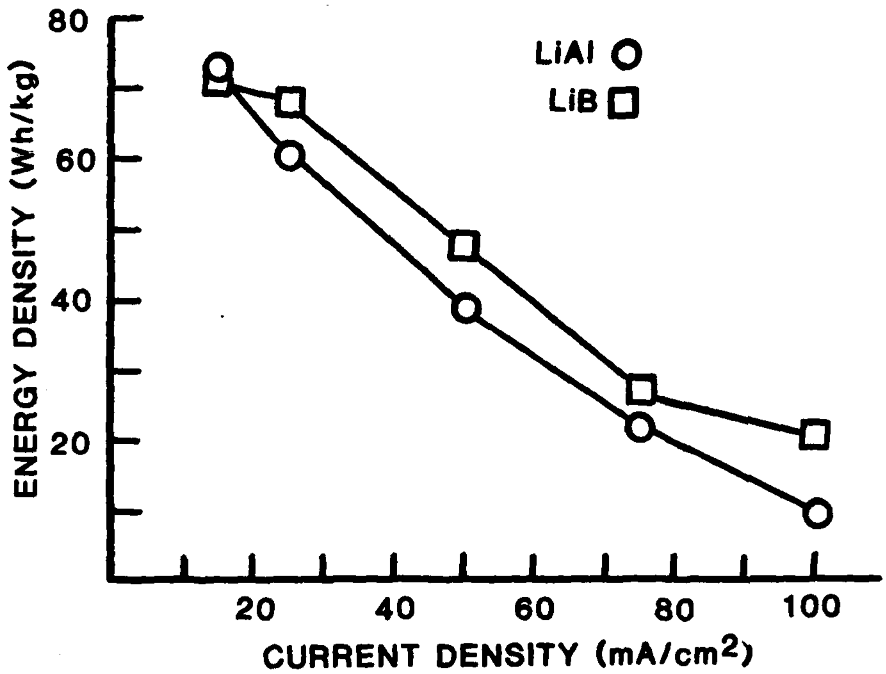

Figure 5. Comparison of energy densities obtained from cells with LiAl and LiB anodes.

difference in anode weights (0.16g LiB versus 0.27g LiAl + 0.12g electrolyte-binder). This LiAl anode was the lightest anode that could be fabricated using our facilities (8). LiB appears to be increasingly better at higher current densities, as the polarization data indicated.

LiSi Anodes.

The experiments using LiSi anodes were complete, therefore the results are more meaningful.

At 200°C, the open circuit potentials were 1.93V for LiSi cells and 1.91V for LiAl cells. These values appear to be about 0.05V higher than would be expected. The source of this increased voltage is not known.

Figure 6 shows the polarization data for LiSi and LiAl cells at 175°C and 250°C. Both type cells show linear polarization with slopes that are essentially the same. The internal resistance at all temperatures are shown below:

	Internal Resistance (Ω)	
Temperature (°C)	LiAl	LiSi
175	0.89	0.96
200	0.32	0.35
225	0.32	0.34
250	0.31	0.28
275	0.29	0.28

The energy densities obtained from LiSi cells are compared with LiAl cells as a function of current density in Figure 7 and as a function of temperature in Figure 8. These figures show that cell performance is essentially the same for both types of anodes at all operating conditions.

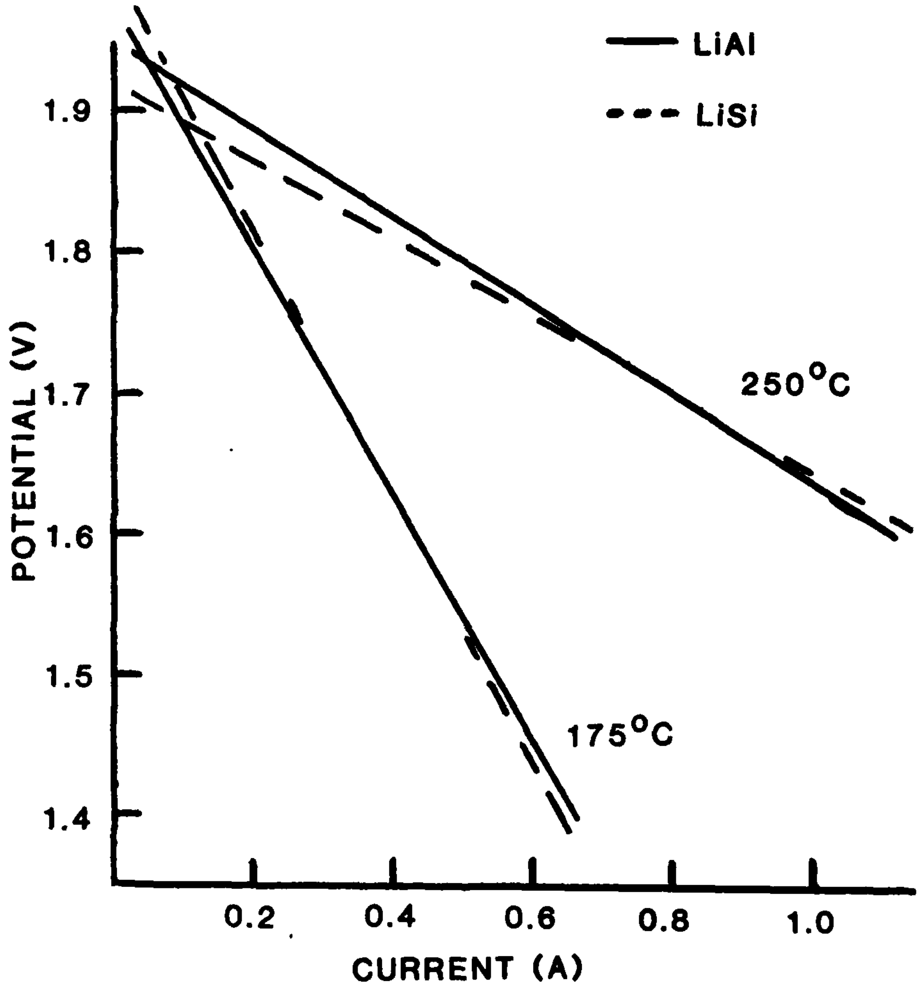

Figure 6. Polarization of chloroaluminate thermal cells with LiAl and LiSi anodes at 175 and 250°C.

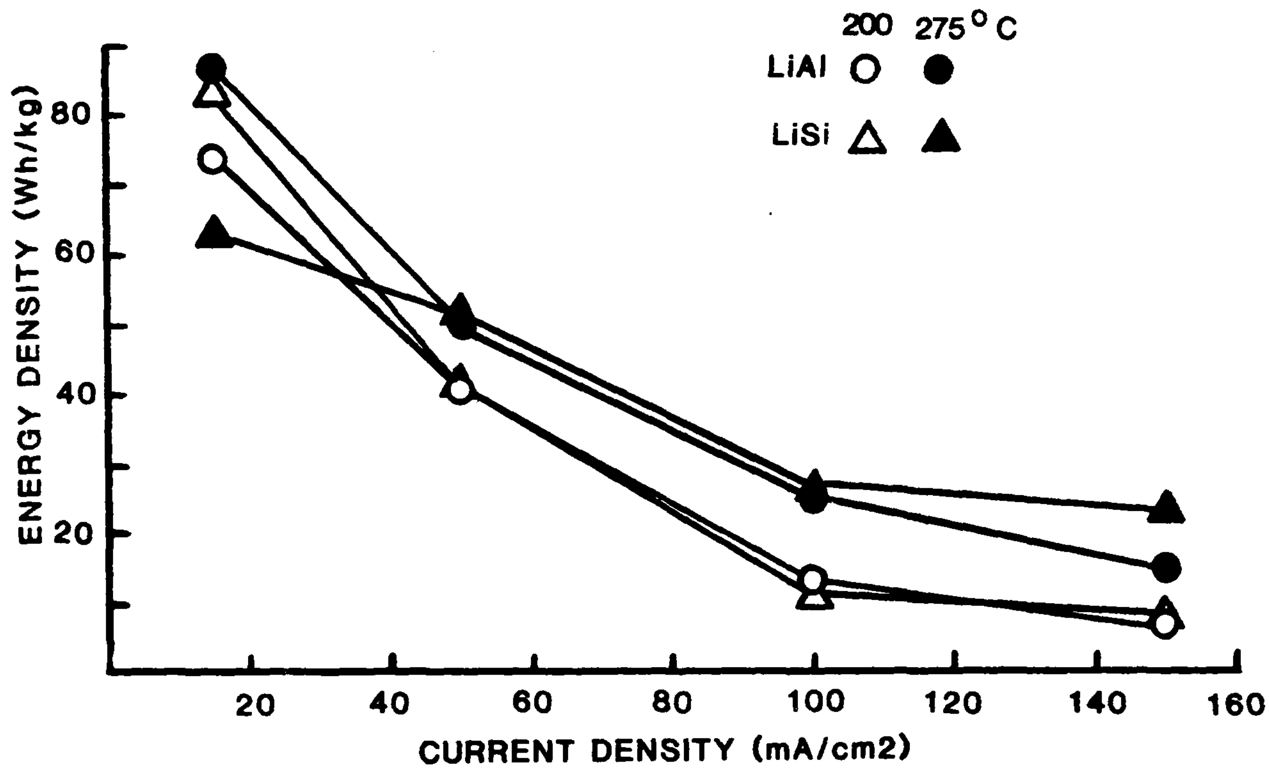

Figure 7. Energy density as a function of current density at 200 and 275°C for thermal cells with LiAl and LiSi anodes.

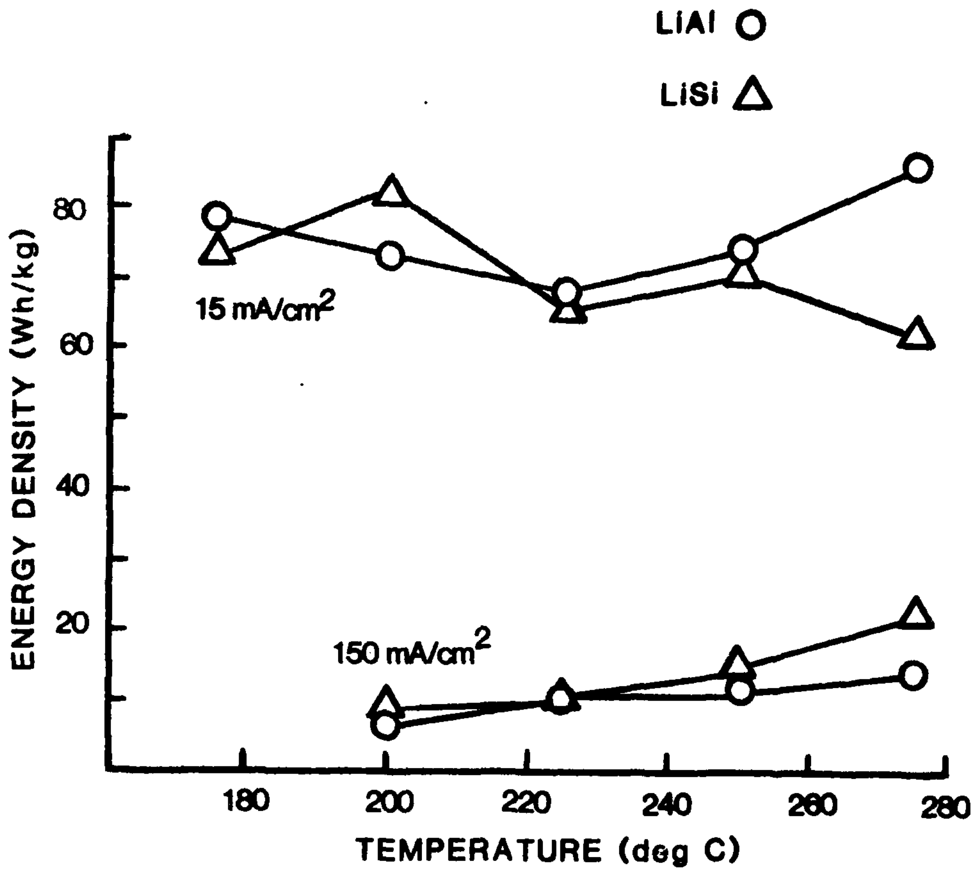

Figure 8. Energy density as a function of temperature at 15 and 150 mA/cm^2 for thermal cells with LiAl and LiSi anodes.

CONCLUSIONS

This study showed that LiSi and LiAl behave much alike as anodes in chloroaluminate thermal cells, whereas LiB behaves quite differently. This is understandable since the physical nature of LiB is considered to be different from the other materials.

The different behavior can be seen in the polarization data for cells with LiAl, LiSi, or LiB anodes. LiSi and LiAl both showed linear polarization for the current densities studied. The internal cell resistances determined from the polarization data were essentially the same for both types of cells at every temperature. On the other hand, cells with LiB anodes exhibited a logrithmic polarization at low current densities, indicating an activation overpotential. Based on the highest current densities used in this study, the polarization data indicate an internal resistance of less than 0.19Ω. From this lower internal resistance, one would expect that LiB should be the superior anode material for high current density operations. The area of high current density will be studied in more detail when LiB becomes more readily available.

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